Local matrix-cluster interactions in a phase separated perovskite

S. R. Giblin,[1,*] I. Terry,[2] D. Prabhakaran,[3] A. T. Boothroyd,[3] J. Wu,[4] and C. Leighton[4]
[1]*ISIS Muon Facility, ISIS, Chilton, Oxon, OX11 0QX, United Kingdom*
[2]*Department of Physics, University of Durham, South Road, Durham, DH1 3LE, United Kingdom*
[3]*Department of Physics, University of Oxford, Oxford, OX1 3PU, United Kingdom*
[4]*Department of Chemical Engineering and Materials Science, 421 Washington Ave SE, University of Minnesota, Minneapolis, Minnesota 55455, USA*

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Magnetoelectronic phase separation plays an integral part in many recent advances in the understanding of correlated electron systems. We have studied the magnetically phase separated material $La_{1-x}Sr_xCoO_3$ and observe unambiguous evidence of magnetic interactions between hole-rich ferromagnetic clusters and the neighboring hole poor matrix. We suggest that this mechanism detected here plays an important role in the rich electrical and magnetic properties of $La_{1-x}Sr_xCoO_3$.

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Research into the origins of colossal magnetoresistance (CMR) in bulk magnetic oxides has been stimulated by potential applications, and has revealed a new understanding of correlated electron systems. Materials showing CMR often exhibit magnetoelectronic phase separation.[1–3] Magnetoelectronic heterogeneity exists where ferromagnetic (FM) metallic clusters are distinct from non-FM insulating regions.[4] Recently there has been considerable interest in $La_{1-x}Sr_xCoO_3$ (LSCO) which clearly exhibits magnetoelectronic inhomogeneity as verified by such diverse techniques as electron microscopy,[5] nuclear magnetic resonance,[6] and small angle neutron scattering.[7] The parent compound $LaCoO_3$ is of interest due to its thermally activated spin state transition from a low spin (LS) $S=0$ state, $t_{2g}{}^6e_g{}^0$, to an intermediate spin (IS) $S=1$ state, $t_{2g}{}^5e_g{}^1$. This occurs because of a direct competition between Hund's exchange energy and the crystal field splitting of the d levels.[8,9] Our recent work has confirmed the theoretical prediction[10] of magnetic exciton formation in bulk $LaCoO_{3-\delta}$ due to the presence of oxygen vacancies.[11] An exciton is a region of Co ions not in the LS ground state, created by a local polarization of Co ions around the oxygen vacancy.[10] This is a similar concept to a magnetic polaron where a hole or electron ferromagnetically polarizes the surrounding antiferromagnetic lattice; an exciton is different as the surrounding magnetic ions are initially in a LS, $S=0$ state. This may be the precursor of magnetoelectronic phase separation that is observed upon doping, i.e., these excitons are directly analogous to the ferromagnetic clusters formed at high x and as such may behave in a similar manner. There is evidence to suggest that the excitons can form in both the LS and IS state, leading to the possibility of interactions between the exciton and the undoped $LaCoO_3$ matrix. Magnetic phase separation is ubiquitous in complex oxides, with formation of FM clusters and a nonmagnetic background being common. Many details of the FM cluster behavior have been identified (e.g., field induced growth, temperature dependence etc.), and high x compositions have recently shown behavior suggesting field induced exchange anisotropy.[12] Although the thermally induced spin state has been observed in lightly doped LSCO ($x<0.08$) (Refs. 13 and 14) *interactions* between the matrix and the Sr clusters have not been identified.

In this paper we present muon spectroscopy and magnetic susceptibility data which provide insight into the development of the magnetic phase separation occurring in LSCO from $x=0$ to 0.20. We demonstrate that in $LaCoO_{3-\delta}$ the magnetic excitons are interacting directly with the undoped Co^{3+} matrix surrounding the excitons as it undergoes a LS-IS transition. The interaction is field dependent indicating that it is frustrated on a local level. The result is further complemented by comparative measurements on LSCO. The composition $x=0.03$ is of significance as this is in the dilute cluster limit. The majority of the material "exists" as the undoped $LaCoO_3$ matrix. Any competing interactions between the hole rich regions and the background material are highlighted and the results are comparable to the investigations into $LaCoO_{3-\delta}$. We suggest that the FM clusters, produced when hole doping with Sr ions, interact locally with the non-FM undoped Co^{3+} "matrix" surrounding the clusters. This mechanism influences the magnetic and electrical properties of LSCO. Such a local interaction demonstrated here may be applicable to other oxide materials exhibiting magnetic phase separation.

Bulk muon spin rotation and relaxation (μSR) experiments were performed at the PSI in Switzerland on the instrument Dolly. μSR is well suited to the exploration of local magnetic correlations, with a sampling radius of $\approx$20 Å. Complementary bulk magnetic measurements were performed while warming from 2 to 300 K in fields up to 5 T using a Quantum Design MPMS SQUID magnetometer. Measurements have been performed upon a single crystal $LaCoO_{3-\delta}$ sample, grown by the floating zone furnace technique, which was used in our previous investigation.[11] Polycrystalline samples of LSCO were prepared using a standard solid state reaction;[15] all samples were found to be single phase using x-ray diffraction.

μSR measurements were performed on $LaCoO_{3-\delta}$ in the zero field (ZF) and transverse field (TF) configurations. The TF measurements can be fitted over the entire temperature range using a relaxation function of the form,

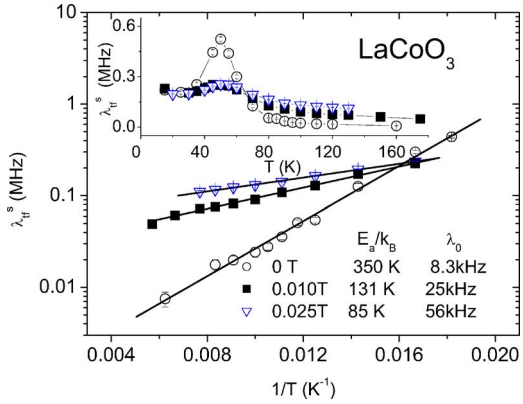

FIG. 1. (Color online) The field dependent depolarization rates as a function of reciprocal temperature (>50 K) for $LaCoO_{3-\delta}$, Arrhenius fits to the data along with the respective fitting components are also shown as described in the text. The inset shows the entire temperature range studied of λ_{tf}^s.

$$G_x(t) = A_{tf}^s \exp(-[\lambda_{tf}^s t]^2)\cos(2\pi\upsilon_\mu t) + A_{tf}^f \exp(-[\sigma_{tf}^f t]^2) + A_{bg}, \quad (1)$$

where A_{tf}^s, A_{tf}^f, and A_{bg} are the initial asymmetries of, respectively, the oscillatory, Gaussian, and background components, and *s* and *f* denote slow and fast relaxing components. The parameters λ_{tf}^s and σ_{tf}^f are the depolarization rates for the two separate decays and υ_μ is the muon precession frequency. No other function was required to fit the TF data. Above 90 K, only the first term in Eq. (1) was required to fit the data, however at lower temperatures the second term begins to dephase the oscillatory component. The total asymmetry over the temperature range investigated remains constant indicating that the additional relaxation below 90 K is a result of paramagnetic species (this process is discussed in depth in Ref. 11). These results were attributed[11] to the spin state transition and magnetic exciton formation, which is a direct result of the IS-LS thermal excitation. An exciton can only form if Co^{3+} ions close to the oxygen vacancy are initially in the LS state.[10] Investigations into the LS-IS transition region by Zobel *et al.*[9] revealed that the rate of Co^{3+} ions undergoing the spin transition as a function of temperature is maximized at about 50 K. Therefore, the requirement of the existence of LS Co^{3+} ions for the exciton formation also suggests that the density of excitons changes rapidly with temperature at 50 K. Below this temperature the majority of the undoped Co^{3+} ion matrix is in a LS state and the number of magnetic excitons would be expected to reach its maximum value, while at temperatures well above the LS-IS transition the number of excitons will be very small. The second term in Eq. (1) was attributed to the depolarization of muons by noninteracting magnetic excitons which were created upon reducing temperature. The first term of Eq. (1) was associated with magnetic excitons which were created within a predominately IS Co^{3+} environment, and thus it is the temperature dependence of λ_{tf}^s that is of interest when considering possible "exciton-non-FM Co^{3+} matrix" interactions.

The inset of Fig. 1 shows the temperature dependence of λ_{tf}^s for both ZF and TF measurements (the ZF relaxation above 50 K is a simple Gaussian decay[11]). Longitudinal field μSR has shown that this relaxation arises from dynamical, fluctuating random local fields.[11] From Fig. 1 it is clear that the depolarization rates peak at 50 K for all fields, but no corresponding bulk magnetic transition can be observed by standard magnetic susceptibility measurements. This can be interpreted as evidence that the exciton becomes the dominant magnetic species as the IS Co^{3+} ions fall into the LS state and that there are no long range magnetic interactions between the magnetic excitons.[9,10] Figure 1 demonstrates that the field dependent depolarization follows a simple Arrhenius thermal activation law of the form $\lambda = \lambda_0 \exp^{E_A/k_bT}$ above 50 K for all measured fields. Moreover, the activation energy decreases with increasing magnetic field while the pre-exponential factor λ_0 increases linearly with field. The high temperature tails of the depolarization rates do not scale with magnetic field, contrary to what might be expected of paramagnetic IS Co^{3+} ions,[7] which should have a field distribution independent of applied field.[18]

Above 50 K it is likely that any exciton that is formed will be surrounded by undoped IS Co^{3+} matrix, leading to a possible interaction between excitons and the surrounding matrix. A Curie-Weiss fit to the magnetic susceptibility data for $100\ \mathrm{K} < T < 500\ \mathrm{K}$ results in a θ value of about −200 K,[16] suggesting a strong AF interaction between neighboring IS Co^{3+} ions. Such an interaction between Co^{3+} ions in the exciton and ions in the surrounding IS matrix could lead to magnetic frustration at a local level. This implies that the muon depolarization rate is effected by the excitons. The excitons will be easily polarized with respect to the field,[11] but the IS Co^{3+} ions surrounding the excitons will be attempting to align themselves in accordance with local AF coupling. The magnetic interaction between the excitons and the surrounding matrix may then be field dependent, leading to an increase in λ_0, the field distribution, and a decrease in activation energy, as the excitons and matrix align with the external field.

This interpretation of the data is based upon the field dependent measurement of the depolarization rate from Fig. 1, however, the Arrhenius fit was performed over a small temperature range and could provide a valid reason for the difference in extracted components. Conversely, our previous work[11] has already shown that it is possible to induce magnetic remanence in the LS temperature region. Specifically, if the sample is field cooled (FC) to 50 K and then the field is removed there is a previously unseen remnant component of the magnetization, that scales with the strength of the cooling field. This cannot be due only to the excitons as no magnetic anisotropy is expected of them.[10] Therefore, the remnant moment (μ) at 50 K can be viewed as a consequence of the exciton interacting with its local environment to create a local anisotropy.

The field cooling dependent μ can be expressed in terms of the activation energy $[E_a(B)]$ obtained from field dependent μSR measurements, in the form, $\mu \propto \exp[E_a(B)/k_BT]$. Figure 2 shows the inverse field dependence of the natural logarithm of the remnant moment at 50 K, suggesting that the remnant moment is indeed a consequence of the IS matrix interacting with some excitons. The interaction is field dependent as determined by μSR measurements. This em-

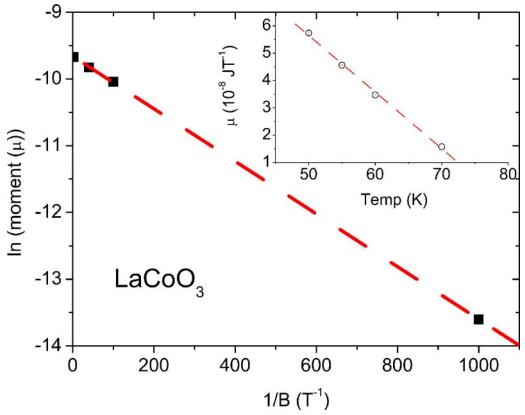

FIG. 2. (Color online) Field cooling dependence of the natural logarithm of the remnant magnetization for $LaCoO_{3-\delta}$ (Ref. 11), as an inverse function of magnetic field, $T=50$ K. The inset shows the temperature dependence of the remnant moment after cooling in a field of 50 m T until the appropriate temperature and then measuring in the remnant field.

pirical observation is further complemented by the inset of Fig. 2 which shows the remnant moment after field cooling in 50 m T until the respective temperature and then measuring in the remnant field of the magnet (10 m T), further suggesting that the remnant moment is dependent upon the applied cooling field.

When $LaCoO_3$ is hole doped with Sr ions FM clusters are known to form. Specifically, the clusters contain Co^{4+} ions and a metal insulator transition (MIT) is observed when the clusters percolate ($x\sim0.17$).[7,17] The possibility of the undoped $LaCoO_3$ matrix contributing to the magnetic properties is generally neglected.[14] Also, no spin glass behavior is observed when $x<0.06$.[7,17] However, μSR is sensitive to the local magnetic environment. TF measurements (10 m T) on the $x=0.03$ sample were performed, and the data can be fitted with Eq. (1) over the entire temperature range, with the second component becoming apparent below 50 K. Figure 3 shows the temperature dependence of the initial asymmetry of the oscillatory component (A_{tf}^s) compared to the derivative of the FC magnetic susceptibility with respect to tempera-

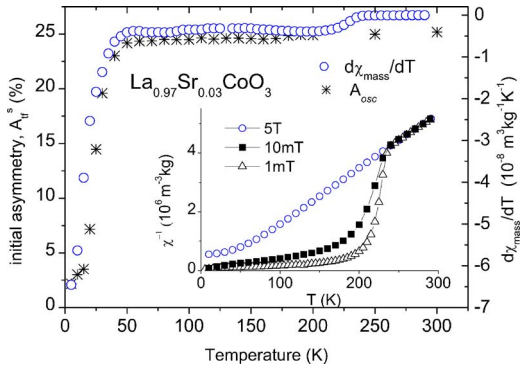

FIG. 3. (Color online) Temperature dependence of the initial asymmetry (A_{tf}^s) of the oscillatory component for the $x=0.03$ sample directly compared to the differential of the FC mass susceptibility. The inset demonstrates the temperature dependent reciprocal mass susceptibility with respect to the measuring field.

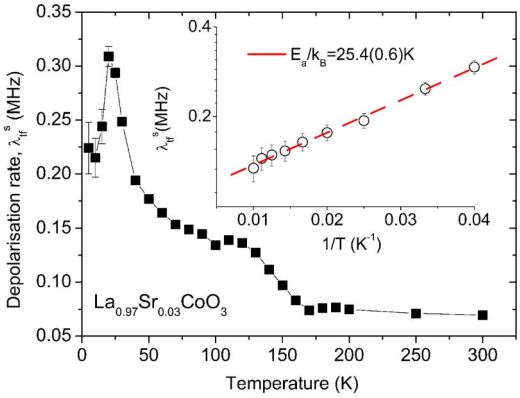

FIG. 4. (Color online) Temperature dependence of the depolarization rates for the $x=0.03$ sample obtained from the oscillatory component in equation (1). The inset shows the inverse temperature dependence of the depolarization rate above 30 K.

ture. This derivative highlights any subtle change in the magnetic response of the sample. There is a clear dephasing of the muons coincident with a change in $d\chi/dT$ below 50 K. A similar response was observed in $LaCoO_3$ as the system underwent the LS-IS transition and was inferred to be due to the increased density of magnetic excitons dephasing the muons.[11] In the $x=0.03$ sample the situation is somewhat different as the doping occurs due to the presence of Sr ions. The drop in A_{tf}^s is coincident with the second Gaussian component being required to fit the data. No change in A_{bg} is seen over the entire temperature range. The inset shows the temperature dependent inverse magnetic susceptibility as a function of applied field. The data cooled and measured in 5 T, 10 m T and 1 m T clearly superimpose above 225 K, and produces a θ value of 3 ± 4 K demonstrating that the material has essentially a (noninteracting) paramagnetic temperature dependence. However, below 225 K the data no longer overlap. The experiments performed were FC, suggesting that the orientation of the local anisotropy field is strongly field dependent, highlighting the role of competing magnetic interactions. One simple origin of this behavior stems from the local AF interactions in the undoped $LaCoO_3$ matrix. If these "random" interactions are enveloping the hole-rich clusters, a field dependent magnetic alignment that results from the interplay between frustrated interactions can be envisaged, where the Co^{3+} HS ions in the cluster (induced by the Co^{4+} ions) are analogous to the magnetic excitons present in $LaCoO_3$. Note the FM intracluster interaction (Co^{4+}-Co^{3+}) will be different to the AF interactions observed in the magnetic excitons in $LaCoO_3$.

If the local ordering of the AF $LaCoO_3$ matrix is interacting with the hole-rich clusters as interpreted from the inset of Fig. 3 then the field distribution will be sensitive to this ordering. Figure 4 shows the temperature dependence of λ_{tf}^s and clearly demonstrates that at about 25 K there is an apparent magnetic transition. No such observation has been made before, and we suggest that here the clusters become dominant. This directly implies that above 25 K the clusters must have been interacting with the undoped $LaCoO_3$ matrix which is undergoing a thermally induced spin transition. The emergence of the noninteracting clusters as a dominant mag-

netic entity occurs at a lower temperature than in Fig. 1, and could be a consequence of different exciton and/or cluster densities or the effect of strain in LSCO closing the spin gap. The inset shows the inverse temperature dependence between 50 and 100 K and the corresponding activated fit. The value of E_a is ~25 K and, for a spin glass,[19] this makes little sense as the fitting range to obtain this energy is $\gg$26 K (also no glassy behavior[21] is observed). Because E_a is less than the fitted temperature range there may be more than one activated process involved in the depolarization of the muons. This can easily be envisaged when considering two competing activation energies E_1 and E_2 (representing the competing magnetic interactions when a magnetic field is applied), of the form, $A\exp(E_2/k_BT)/B\exp(E_1/k_BT) = C\exp[(E_2-E_1)/k_BT]$ where A, B, and C are constants. The activation energy of $LaCoO_3$ when applying a TF field of 10 m T has already been calculated to be 131 K (Fig. 1), and this field dependent activation energy was related to the coupling between the magnetic excitons and $LaCoO_3$ matrix. Considering the $x=0.03$ sample, it is feasible to acknowledge the presence of undoped $LaCoO_3$ regions interacting with the induced HS Co^{3+} ions which form part of the hole-rich clusters; the similarity of the two systems suggests that E_2/k_B can be assigned a value of 131 K. Assuming the resulting activation calculated in Fig. 4 is 25 K (from the Co^{4+}-Co^{3+} cluster interaction), E_1/k_B takes a value just over 110 K. In this temperature regime a shoulder in λ_{tf}^{s} is observed in Fig. 4. This suggests that the muons appear to be sensitive to the undoped local $LaCoO_3$ and to the exchange between thermally activated Co ions surrounding the hole-rich clusters, a LS-IS transition in $x=0.03$ is being observed. Note the transition is not observed in bulk measurements because its contribution to the total magnetic susceptibility is several orders of magnitude smaller than even a 1% contribution from FM Sr rich clusters.[11]

We have performed complementary zero field μSR measurements on LSCO samples around the MIT, concentrating on the $x=0.15$ and 0.20 samples which support the interpretation of cluster-matrix interactions presented in this work. Specifically no muon precession frequency was observed in $x=0.20$ (the FM region), in agreement with previous work on a $x=0.30$ sample[20] and the known spin glass behavior was not observed with muon spectroscopy[21] in the $x=0.15$ sample. Both sets of data can be fitted at all temperatures with an exponential relaxation of the form; $G_z(t) = A\exp[-(\lambda t)]+A_{bg}$. The behavior of the relaxation in the $x=0.20$ sample is not what is expected for a true FM ordering of the bulk, suggesting that the hole-rich clusters are undergoing local interactions. Figure 5(a) shows the temperature dependence of the A for both $x=0.15$ and 0.20 compared directly to the FC dc magnetic data of the samples. The gradual dephasing in the $x=0.15$ sample is seen to clearly occur, beginning at 220 K. The drop in the initial asymmetry clearly tracks the increase in magnetic susceptibility suggesting that, below 220 K, the muons are being dephased by local perturbations that induce local magnetic order; this behavior has been previously attributed to the matrix interacting with the excitons or clusters for the case of $x=0$ and 0.03, respectively. The muon data shown in Fig. 5 can be

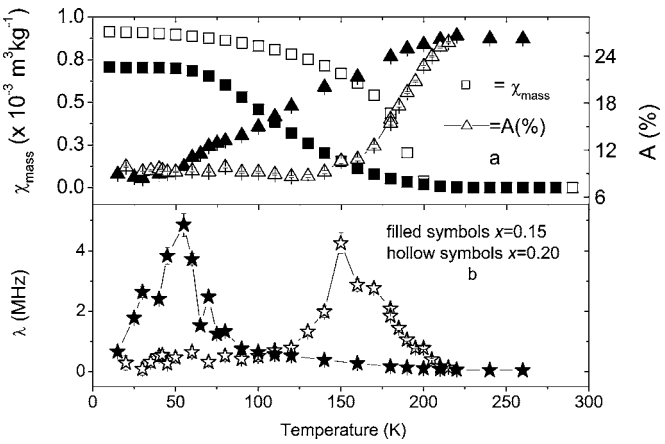

FIG. 5. (a) Temperature dependent comparison of the susceptibility (squares) and initial asymmetry (triangles) of the $x=0.15$ (filled) and 0.20 (hollow) samples. (b) The temperature dependence of the depolarization rates (λ) for the two samples.

interpreted with this model also assuming matrix-cluster interactions. Above the percolation limit the muons still dephase indicating that the matrix still contributes to the magnetism even though there is contact between clusters. The local matrix interactions moderate the cluster ordering, which explains why all the samples investigated dephase below 220 K, and a similar drop in the asymmetry is observed for the $x=0.30$ composition.[20]

Figure 5(b) also directly compares the temperature dependence of the depolarization rates (λ) for the $x=0.15$ and 0.20 samples. The depolarization rate at the respective transitions are the same for both samples within the error bars, giving a clear indication that the field distribution of the muons does not alter through the percolative metal insulator transition. This is an important result as it indicates that the muons are sampling the hole-rich clusters (implied from the observed transition temperatures), and that the interaction between the clusters does not change through the MIT. Therefore it appears that the muons are detecting the known magnetic phase separation, however the matrix is moderating the magnetic response upon a local level. Both peaks are extremely broad with the $x=0.15$ sample showing an increase in λ below 220 K; however, as noted above, this relaxation is not activated or representative of a spin glass transition.[21] This indicates the importance of the undoped $LaCoO_3$ matrix interacting with the clusters even in the high doping regime.

In summary we have clearly demonstrated evidence for exchange between the HS exciton and the undoped Co^{3+} ion matrix in $LaCoO_{3-\delta}$. Moreover in the phase separated material LSCO we have observed the IS-LS transition of the undoped $LaCoO_3$ matrix at low x. The presence of an undoped $LaCoO_3$ matrix clearly has a profound effect upon the properties of the magnetic clusters present in the $x=0.03$ sample, which appear to be weakly exchange coupled on a local level. Our results also demonstrate the importance of the $LaCoO_3$ matrix for compositions close to the percolative MIT. This observation of local exchange interactions between FM regions and non-FM regions could be applicable to CMR materials.

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*Electronic address: s.r.giblin@rl.ac.uk

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